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ENERGETICS AND COLLISION DYNAMICS OF ELECTRONIC TRANSITION LASE--ETC(U)

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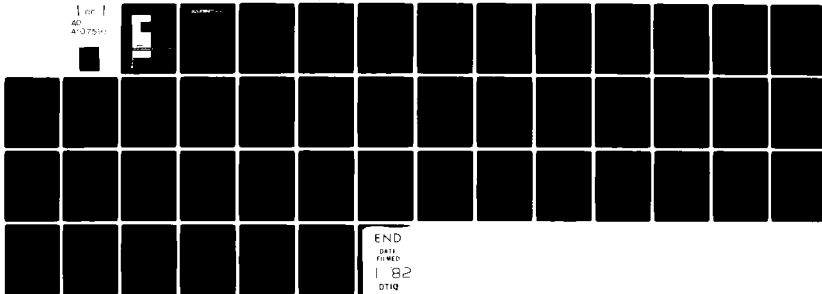
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The research performed under this contract was directed toward the calculation of the electronic structure of selected chemical systems in order to determine their potential as laser systems. An extensive study of the low-lying symmetries of I₂(^{1,3}Σ_{g,u}, ^{1,3}Π_{g,u}, and ^{1,3}Δ_{g,u}) within a relativistic density functional framework was undertaken. Analysis of the components of the low-lying ³Π_u state were of primary concern. Detailed <u>ab initio</u> calculations have been carried out for the low-lying states (²Σ and ²Π) of LiCa, LiMg, and NaMg.		

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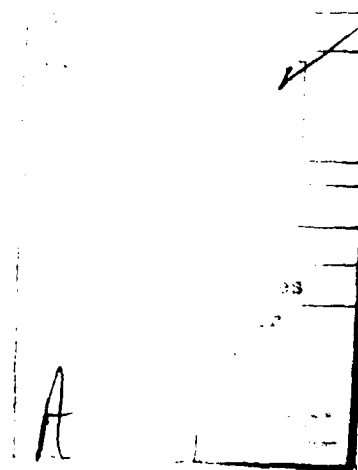
In addition to the studies on the Group IA/IIA systems, an analysis of the quenching of metastable Mg atoms by collision with a noble gas was undertaken. Ab initio calculations of the low-lying electronic states ($1,3\Sigma$, $1,3\Pi$) have been carried out for the MgAr and MgKr systems.

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FOREWORD

This report was prepared for the Air Force Office of Scientific Research, United States Air Force by the United Technologies Research Center, East Hartford, Connecticut, under Contract F49620-80-C-0095, Project-Task No. 2303/B1. The performance period for the technical program was from 1 August 1980 through 31 July 1981. The project monitor was Captain William G. Thorpe, USAF.



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R81-925293

Energetics and Collision Dynamics of
Electronic Transition Lasers

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ABSTRACT

Knowledge of the partition of energy between the products of a chemical reaction is fundamental to the understanding of the dynamics of collisional reactions. Atom-atom and atom-molecule reactions that yield vibrationally excited diatomic molecules are of particular scientific and military interest. An understanding of the dynamics of the simplest of these reactions is a prerequisite for understanding more complicated gas phase reactions. A knowledge of at least limited regions of potential energy surfaces is of importance in analyzing the vibrational and rotational relaxation rates and can be utilized in a predictive fashion. In the low energy regime there are little data available on collision processes and experimental measurements are difficult. Thus, a program to develop theoretical techniques and construct computer programs for calculating potential energy surfaces and kinetic cross sections for simple collision processes is appropriate. The potential energy surfaces include both atom-atom and atom-diatom systems with special emphasis on molecular reactions yielding electronically excited products which have potential as visible or UV chemical lasers. These systems include metal oxides and halides, metal excimers and the noble gas-halides. This research developed techniques and computational schemes for a priori prediction of the kinetics and the product distribution of atom-diatom reactions. This involved (1) improved calculation techniques for potential energy surfaces for the reactants and products, (2) quantum and classical mechanical calculations of the dynamics of the reaction and (3) detailed calculations for systems with high potential as electronic transition lasers.

R81-925293

Energetics and Collision Dynamics
of Electronic Transition Lasers

STATEMENT OF WORK

a. Perform a theoretical research investigation of the electronic structure and energetics of molecular systems and on chemical reactions in such systems which would yield a sufficient density of excited electronic species capable of lasing on an electronic transition. This investigation will include the calculation of electronic wavefunctions and energies as a function of internuclear separation followed by calculations of electronic transition moments for systems selected as typical of this class, and which appear to offer a high potential as candidate lasers. In addition, research shall be carried out related to the development of practical computational techniques for prediction of the kinetics and the product distribution of chemical reactions involving electronically excited reactants or products. Experimental data will be iteratively examined and integrated with the results generated from this theoretical investigation. The computations shall be carried out using density functional and ab initio methods, using computer codes developed or modified at this Center. Specifically, this investigation shall comprise the following:

(1) A survey of existing experimental and theoretical data available to the contractor pertaining to candidate laser systems.

(2) The contractor shall perform quantum mechanical calculations of the electronic wavefunctions, electronic transition moments, and radiative lifetimes for three (3) molecular systems. These systems shall be chosen from the following: I_2 , MgO, BO, and MgCa.

REVIEW OF TECHNICAL EFFORT

Calculations of the dynamics of molecular collisions are ordinarily carried out with the aid of the Born-Oppenheimer separation of the electronic and nuclear motion. One proceeds by calculating the electronic energy as a function of the positions of the nuclei, which are assumed to be stationary. This electronic energy, plus the electrostatic repulsion between the nuclei, defines a potential energy hypersurface on which the nuclei may be regarded as moving. A potential energy hypersurface defined in this way is referred to as adiabatic, and is appropriate for describing the nuclear motion in the limit of low velocity. There are many collisions for which an adiabatic potential energy hypersurface provides an adequate description. However, most reactive collisions and many collisions which do not lead to reaction are inadequately described by an adiabatic potential energy hypersurface. These collisions are characterized by velocities of nuclear motion sufficient to affect adversely the Born-Oppenheimer separation, with the result that the overall wavefunction must be described as a superposition of terms involving different electronic energy states. Under these conditions, it will be useful to consider adiabatic potential energy hypersurfaces corresponding to all electronic states relevant to the overall wavefunction.

When the different potential energy hypersurfaces are well separated in energy, the nuclear motion can ordinarily be described in terms of motion on a single hypersurface. However, when two or more hypersurfaces are close in energy, they can be expected to mix appreciably in the overall wavefunction, and it will then be necessary not only to calculate the hypersurfaces but also to calculate the quantities needed to discuss their mixing in the overall wavefunction.

The calculation of a point on a potential energy hypersurface is equivalent to calculating the energy of a diatomic or polyatomic system for a specified nuclear configuration, and therefore will present considerable practical computational difficulty. For certain problems or nuclear configurations, the maximum possible accuracy will be needed and under these conditions relatively elaborate ab initio methods are indicated. Under other conditions, it may be possible to use less elaborate and more rapid computational methods, and density functional or other approaches may then prove useful.

A knowledge of at least limited regions of potential energy surfaces is of importance in analyzing the electronic, vibrational and rotational relaxation rates in chemical laser systems. These relative relaxation rates govern the feasibility of lasing and the power that is potentially available. Relaxation rates are governed by long-range forces between atomic and

molecular fragments and thus knowledge of the dissociation behavior represented by the potential energy surfaces for the laser system can be used in calculations of the kinetic behavior.

Our research effort to date has been devoted to the theoretical development of computational techniques for the prediction of potential energy surfaces, and to studies of the energetics of prototype electronic transition laser systems, the prediction of the radiative lifetimes of electronically excited species, and studies of photon energy loss paths such as photoabsorption or ionization of the upper excited electronic states. The goal of this research program is to develop a technical information base in support of the development of a practical chemical laser system operating on an electronic transition.

RESEARCH PROGRESS DURING THE CONTRACT PERIOD

For several years this Center has been involved in detailed ab initio quantum mechanical studies of the electronic structure, radiative, and kinetic properties of diatomic and polyatomic molecules. These studies have focused on air molecules and metal oxides, with applications to weapons technology, and on species which show promise as candidate laser molecules.

Our initial quantum mechanical studies dealt with the electronic structure and radiative lifetimes of the air system and certain diatomic metal oxide species which may be of abundance in the perturbed atmosphere following a thermonuclear explosion. Such diatomic species commonly exhibit strong LWIR radiation and a quantitative measure of this effect is needed to analyze the atmospheric kinetics. These studies were carried out using methods of molecular quantum mechanics coupled with available spectroscopic information on excited electronic states.

As an outgrowth of this research, a narrower study of certain classes of metal oxides and halides was initiated with the intent to screen such systems for candidates which might show potential as visible or UV electronic transition lasers. The criteria were to uncover systems having a low-lying excited state with a reasonably long radiative lifetime and situated energetically such that an inversion of population with respect to the dominant transitions to the ground state was possible. The systems under investigation to date include the group IIA metal oxides (BeO-BaO), the group IVB metal fluorides (SiF, GeF, SnF), the group IVB metal oxides (SiO-PbO), NF, MgF, AlF and the thirteen electron sequence: N_2^+ , CN, BO and BeF. These last systems have a common chemistry of their electronically excited states including a common $A^2\Pi \rightarrow X^2\Sigma^+$ Meinel transition, $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ first negative transition and a possible metastable $a^4\Sigma^+ \rightarrow X^2\Sigma^+$ transition.

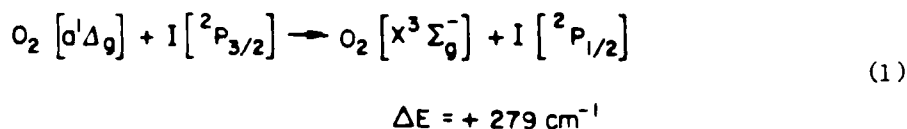
As a result of these investigations, which were mainly carried out under Air Force sponsorship, this Center has available a large data base of calculated electronic energies and transition probabilities for metal oxide and halide systems. This base includes calculations for the ground and many electronically excited states of these molecules. Several of these systems have been analyzed in detail and their potential as candidates for electronic transition lasers has been evaluated (Refs. 1-5). These studies form a sound basis for analysis of such molecules as candidate laser systems. To the best of our knowledge, no other laboratory in the country has such an extensive catalogue of theoretical calculations of the electronic structure of metal oxides and halides or our computational experience with these types of molecules. In addition, UTRC has fully developed sophisticated computer programs for studying both diatomic and polyatomic molecules. These programs have been extensively used at UTRC and at the Air Force computational laboratories at AFWL, Kirtland Air Force Base and AFGL, Hanscom Field.

In addition to our studies of metal oxide and halide systems, a parallel theoretical research effort was directed toward analyzing the electronic structure of excimer laser systems. This program was concerned with a study of the energetics of the noble gas halides and noble gas dimer and trimer molecular ions and studies of candidate noble gas laser molecules operating on an electronic transition. The emphasis of the study of the noble gas halides was on the definition of potential energy curves, prediction of the radiative lifetimes of electronically excited states, and studies of photon energy loss paths such as photoabsorption and photoionization of the upper excited electronic states. A major effort of the study of the noble gas dimer and trimer ions was the definition of the potential energy curves and prediction of the photoabsorption cross-section for these species. Several of these systems have been evaluated in detail and the results have been reported in technical articles (Refs. 6-12).

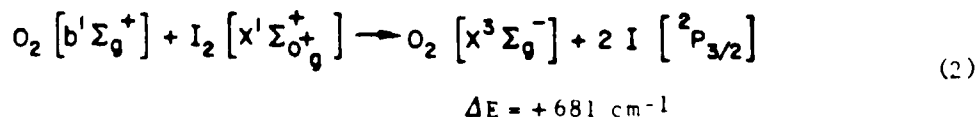
As a continuation of our theoretical research studies of the energetics and collision dynamics of electronic transition - chemical laser systems, a research program to calculate the electronic structure and radiative properties of the I_2 , LiCa, LiMg, MgCa and MgRg (Rg = noble gas) molecules was undertaken. These particular molecules were chosen because of their current AF interest as candidate laser systems or as species of importance in the kinetics of such systems. A review of our results for each separate molecular system is listed below.

I_2

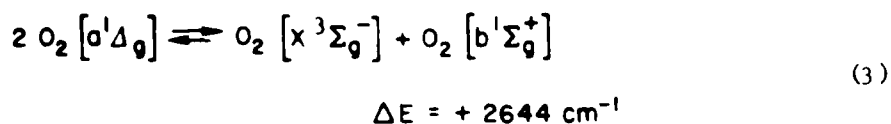
The chemical excitation of iodine through energy transfer with O_2 ($^1\Delta_g$) occurs by means of the efficient, near-resonant exchange reaction:



The production of ground state atomic iodine was originally thought to proceed through the reaction:

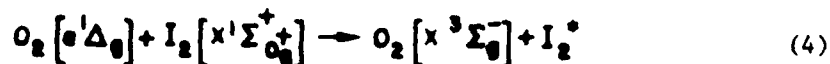


and that this reaction was driven by the $b^1\Sigma_g^+$ state of O_2 produced in the energy pooling reaction:

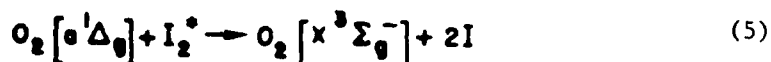


However, recent studies have shown (Ref. 13) that this energy pooling reaction proceeds much too slowly to be of major importance in the I_2 dissociation kinetics.

Recent modeling analysis of the I_2 dissociation kinetics (Refs. 14 and 15) suggests that a low-lying excited state of I_2 must be involved in the reaction mechanism. These models suggest the following reaction steps:



where I_2^* is either a low-lying electronic state of I_2 or possibly the ground electronic state of I_2 in a high vibrational level ($v'' \sim 40$). The second reaction step involves collision of I_2^* with a second $O_2 [a^1\Delta_g]$ molecule:



The evidence to date is still unclear, but the interpretation of Eq. (4) as the production of highly vibrationally excited ground state I_2 is unlikely since experiments show no observable changes in the reaction rates under conditions which should be effective in collisionally deactivating I_2^* . An alternate interpretation is that I_2^* really represents a low-lying metastable state of I_2 that can be reached via reaction (4).

The most likely possibility is that I_2^* represents the low-lying $A' [^3\Pi_{2u}]$ state of I_2 which is not radiatively connected to the ground state and should exhibit metastable behavior. Recent spectroscopic studies by Tellinghuisen (Refs. 16 and 17) place this state too high to be energetically accessible by $O_2 [a^1\Delta_g]$ but the symmetry identification of the state observed in his experiments is uncertain and other experimental studies of multi-photon absorption in I_2 (Refs. 18 and 19) suggest that this $[A' ^3\Pi_{2u}]$ state lies much lower in energy than previously thought ($T_e \approx 7600 \text{ cm}^{-1}$).

We have undertaken an extensive study of the I_2 molecule within a relativistic density functional framework. A correlation diagram for I_2 is shown in Fig. 1 with both (Λ , S) and (J, J) couplings indicated. Of primary concern is the analysis of the components of the low-lying $^3\Pi_u$ state. Since I_2 is a heavy-atom molecule, the importance of relativistic effects must be analyzed. In Fig. 2, we show a comparison of our calculated eigenenergy spectra for I and I_2 in a non-relativistic (NR), a relativistic (R), and a relativistic spin-polarized (RSP) framework. These data indicate that the 5p electrons in I_2 are essentially non-relativistic in character, both in the atomic limit and in the outer valence MO's. This arises owing to a balance of effects of the contracted 5s orbitals and the anti-shielding effects of the 4d orbitals. A second observation is that there is little s-p hybridization in the outer valence character of I_2 since the 5s orbitals lie significantly lower than the 5p orbitals in energy. A further confirmation of these conclusions is given in Fig. 3 which shows that the ground state of I_2 is described uniformly in either a relativistic or non-relativistic treatment.

A bond order analysis of I_2 is shown in Table 1 which indicates that the $^3\Pi_u(\Lambda, S)$ coupled state arising from the $2431 (2\sigma^2 1\pi^4 1\pi^3 3\sigma)$ configuration should exhibit bonding character. Detailed density functional calculations were carried out for this symmetry within a (Λ, S) coupled framework. The spin-orbit splitting of this state was treated perturbatively as indicated in Table 2, where only one-center contributions to V^{SO} are included. This clearly is the weakest link in our analysis of this system. We find the $^3\Pi_{2u}(J, J)$ coupled component of this state to be low-lying, in essential agreement with the evidence of Kawasaki, et al (Ref. 19).

A summary of the spectroscopic analysis of several low-lying states of I_2 is given in Table 3 where we find that the $A' ^3\Pi_{2u}$ state is very similar to the known $B ^3\Pi_{0+}$ state of I_2 . It should be emphasized that these calculated data

for $I_2 [A' ^3\Pi_{2u}]$ are of a preliminary nature and further studies of the spin-orbit coupling effects in progress. A suggested mechanism for I_2 dissociation is given in Table 4. The validity of these several reaction steps is under further study.

Group IA/IIA Molecules

A correlation diagram for several of the Group IA/IIA molecules is shown in Table 5. Detailed ab initio CI calculations have been carried out for the LiCa, LiMg, and NaMg systems. The results obtained to date are summarized below.

LiCa

Ab initio configuration-interaction calculations have been performed for the LiCa molecule. The spectroscopy of this molecule has been studied at AFWL and our calculations are in support of this experimental effort. Our calculated potential energy curves for LiCa are shown in Fig. 4 where it is seen that the ground $X^2\Sigma^+$ state exhibits weak binding and the low-lying $A^2\Pi$ and $B^2\Sigma^+$ states are bound by nearly 0.8 eV. The calculated spectroscopic constants for this molecule are given in Table 6. An analysis of the composition of the VCI wavefunction for this molecule and examination of the calculated dipole transition moments clearly indicate that the $A^2\Pi$ and $B^2\Sigma^+$ states have a diabatic origin of $Li(^2S) + Ca^*(^3P)$ and that a strong homogeneous mixing occurs for internuclear separations in the region near 4.0 Å. Thus the observed binding of the $A^2\Pi$ and $B^2\Sigma^+$ states in LiCa has origin in the chemically reactive 3P state of calcium. The calculated photoemission spectra for LiCa is shown in Table 7 and a comparison of our calculated and the AFWL experimental spectrum is given in Fig. 5. The agreement is excellent clearly indicating that the spectra are due to the $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ band system.

MgNa

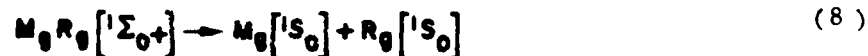
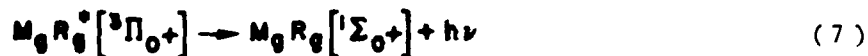
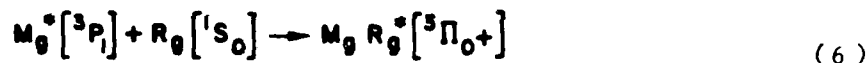
The low-lying doublet sigma and pi states of MgNa have been studied in detail. A correlation diagram for the low-lying molecular states of MgNa and their dissociation limits is shown in Table 8. Ab initio calculations were carried out on the $^2\Sigma$ and $^2\Pi$ symmetries. These states are presented in Fig. 6.

LiMg

A correlation diagram for the low-lying molecular states of LiMg and their dissociation limits is shown in Table 9. Ab initio configuration-interaction calculations have been performed for this molecule. The potential energy curves for the ground and low-lying excited states are presented in Fig. 7.

MgRg

In addition to our studies of the Group IA/IIA systems, an analysis of the quenching of metastable Mg atoms by collision with a noble gas was undertaken. A correlation diagram for intermediate coupling of these molecules is given in Fig. 8. The spin-orbit coupling matrices for the low-lying manifold of states are shown in Table 10. Ab initio calculations of the low-lying electronic states have been carried out for the MgAr and MgKr systems. The calculated potential energy curves are shown in Figs. 9 and 10, respectively. For both systems, the $^1\Sigma_0^+$ component dominates the collisional deactivation kinetics. Further studies of these systems, including an analysis of radiative coupling in the reaction



are in progress.

PUBLICATIONS AND PRESENTATIONS

The significant research results obtained under this Contract have been prepared for publication in technical journals or presented at technical meetings. These papers and meeting are listed below. Abstracts of several of the published papers are included in the Appendices to this report.

A. Technical Reports in Journals and Books

1. "Electronic Structure of Noble Gas Dimer Ions, III. Absorption Spectrum for the $A^2\Sigma_u^+ - B^2\Pi_g$ System." H. H. Michels and R. H. Hobbs, to be published in the Journal of Chemical Physics.
2. "Electronic Structure and Photoabsorption Properties of Noble Gas Trimer Ions." H. H. Michels and R. H. Hobbs, to be published in the Journal of Applied Physics.
3. "Laser Chemiluminescence of LiCa." D. K. Neumann, D. J. Benard and H. H. Michels, Chemical Physics Letters, Vol. 73. 343-347, 1980.
4. "Potential Energy Surface and Cross-Sections for the $H^-(D^-) + H_2(D_2, HD)$ Ion-Molecule Reactions." H. H. Michels and J. F. Paulson, Published as Chapter 22 in Potential Energy Surfaces and Dynamics Calculations, D. G. Truhlar, ed., Plenum Press, New York, 1981.
5. "Electronic Structure of Low-Lying Excited States of I_2 ." H. H. Michels and R. H. Hobbs, to be published in Chemical Physics Letters, 1982.
6. "Laser Chemiluminescence of NaMg." D. J. Benard and H. H. Michels, Chemical Physics Letters, in press.

Technical Paper and Lecture Presentations

1. "Potential Energy Surface and Cross-Sections for the $H^-(D^-) + H_2 (D_2, HD)$ Ion-Molecule Reactions." Presented at the American Chemical Society Meeting, Las Vegas, Nevada, 25-29 August, 1980.
2. "Theoretical Studies of the Energetics and Spectroscopy of Candidate Laser Systems." Presented at the AFOSR Contractors' Meeting, Air Force Geophysics Laboratory, Hanscom AFB, Massachusetts, 8-10 October 1980.
3. "Theoretical Studies of the Spectra of Heavy Atom Molecules." Presented at the American Conference on Theoretical Chemistry at the University of Colorado, Boulder, Colorado, 22-26 June 1981.
4. "Spherical Harmonic Expansion Techniques for Multicenter Integrals over STO's. A Reexamination for Vector Processing Computers." Presented at the Workshop on Multicenter Integrals, Tallahassee, Florida, 3-6 August 1981.
5. " I_2 Calculations." Presented at the Workshop on I_2/O_2 Dissociation Kinetics, Albuquerque, New Mexico, 10-11 September 1981.

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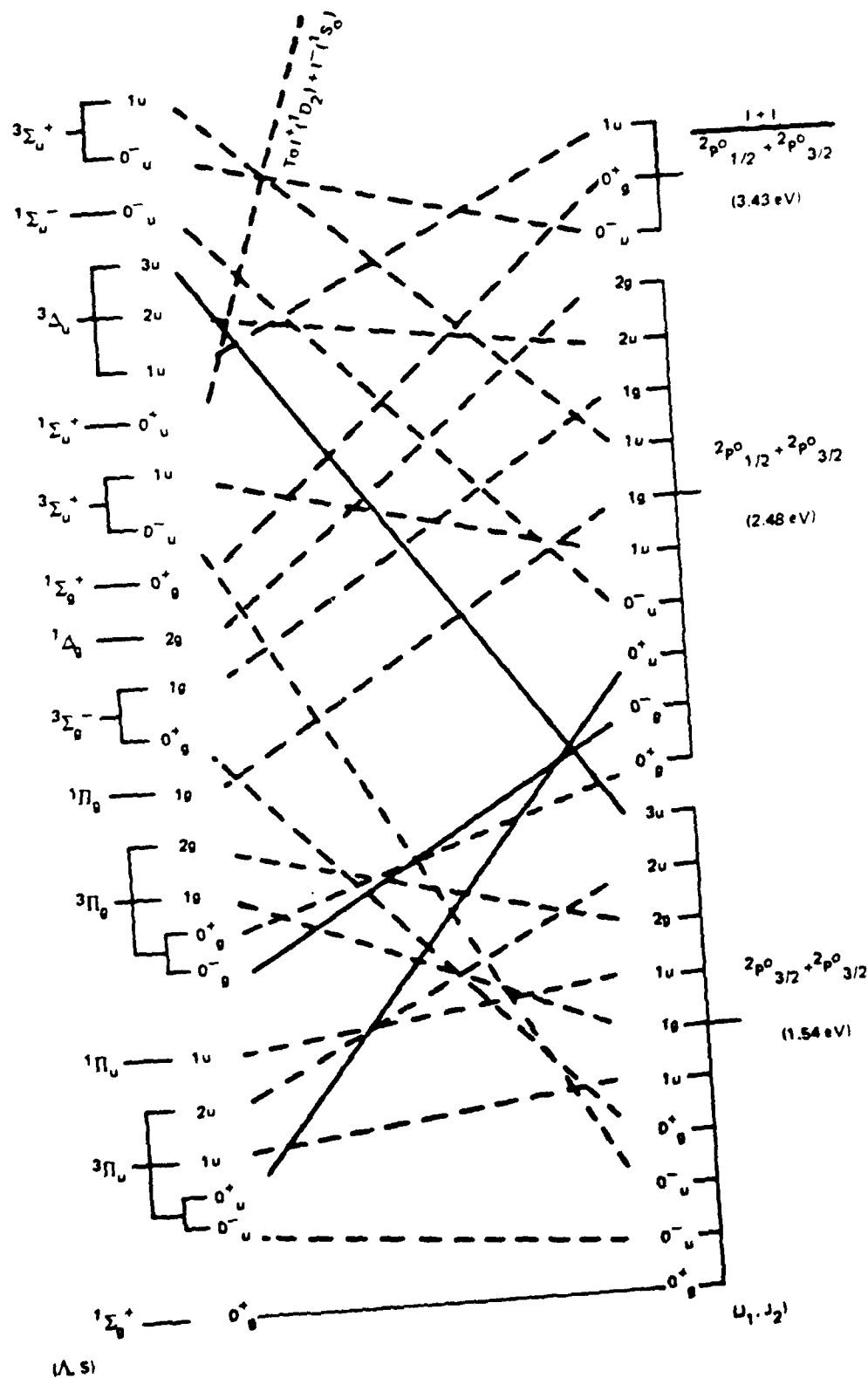
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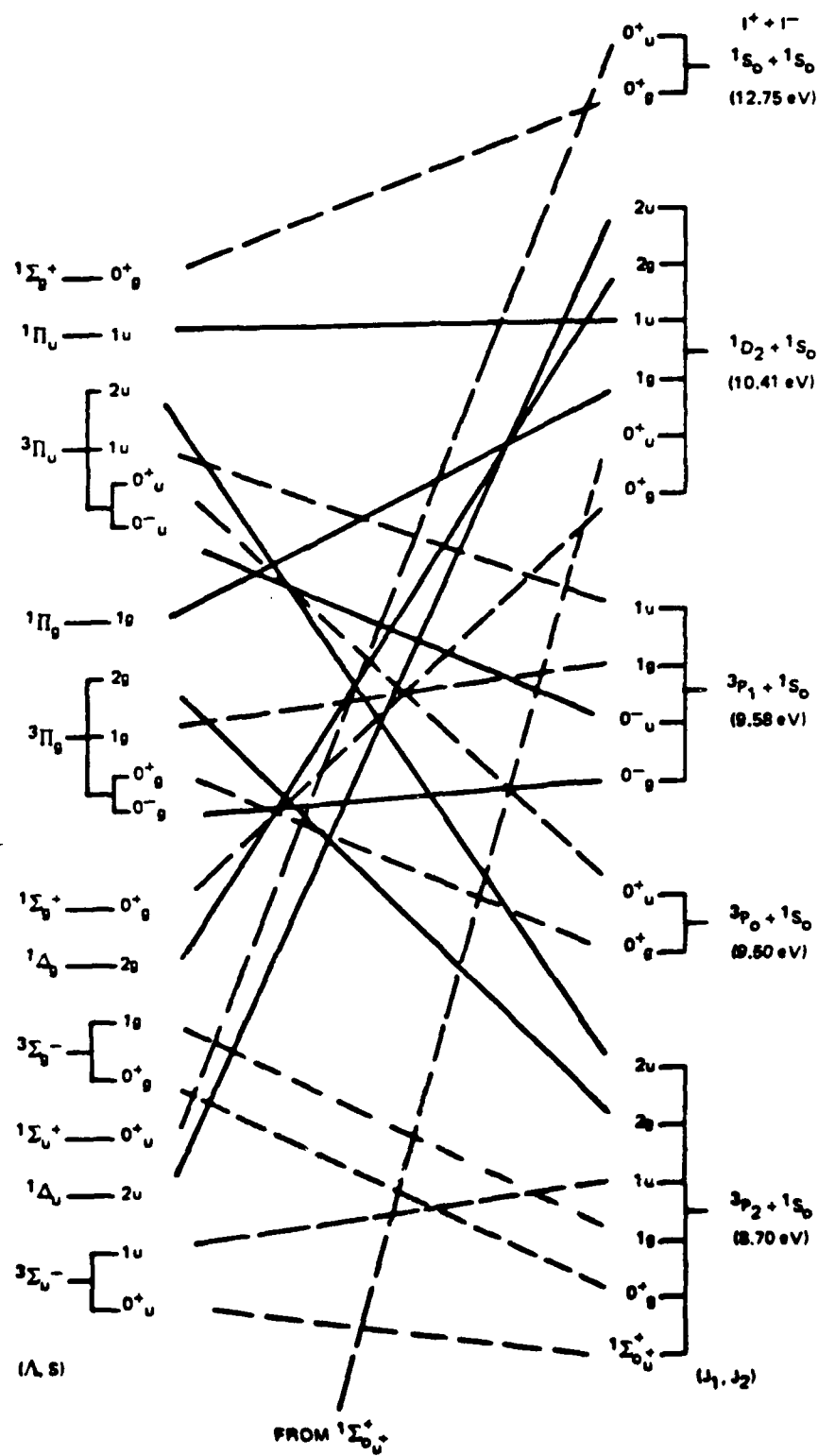
FIG 1

CORRELATION DIAGRAM FOR INTERMEDIATE COUPLING OF THE I₂ MOLECULE

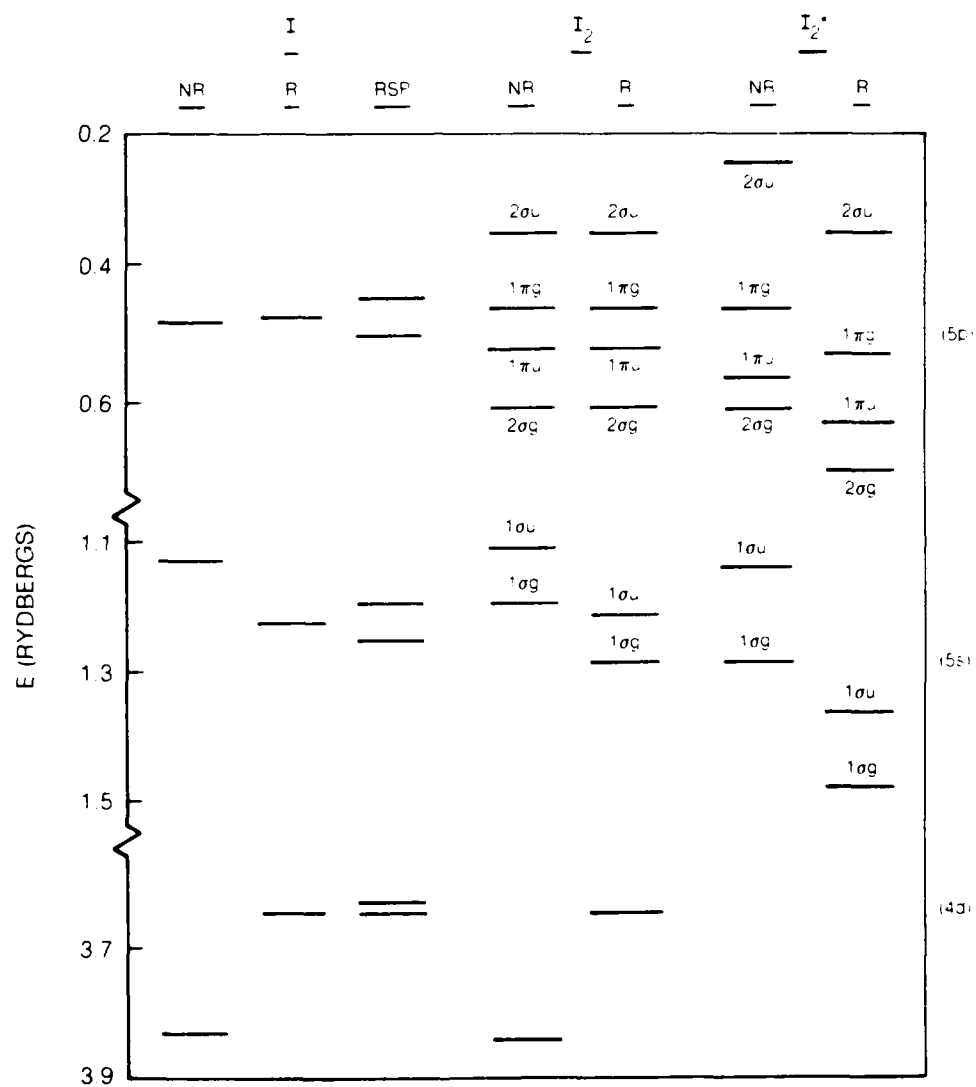
UNIQUE ASSIGNMENTS FROM (J₁, J₂) TO (Λ, S) COUPLING ARE INDICATED BY SOLID LINES



81-9-98-1



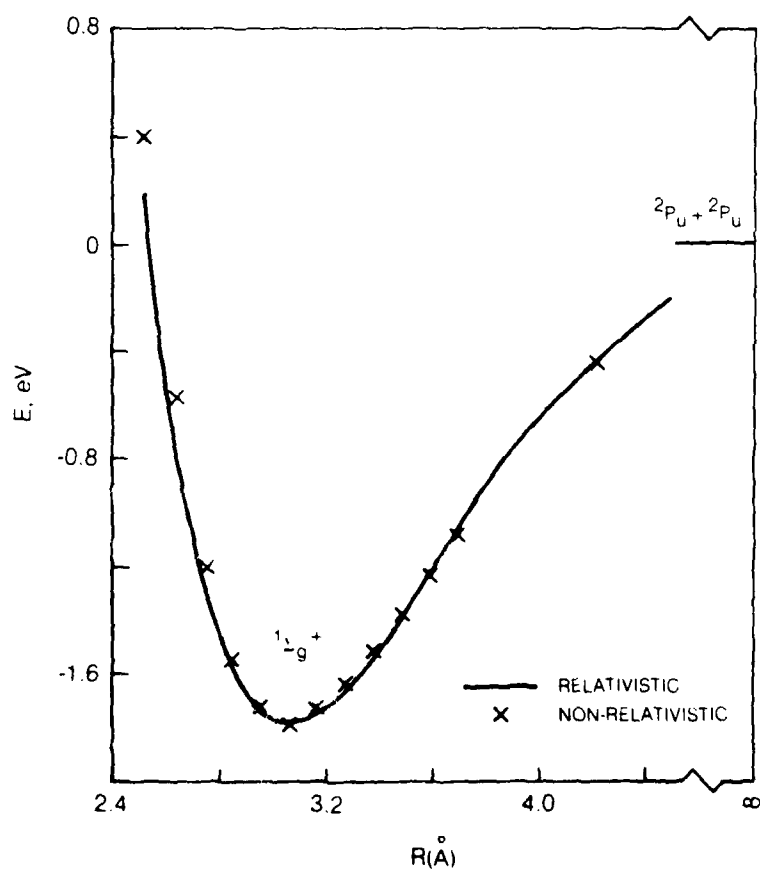
NON-RELATIVISTIC AND RELATIVISTIC BINDING ENERGIES



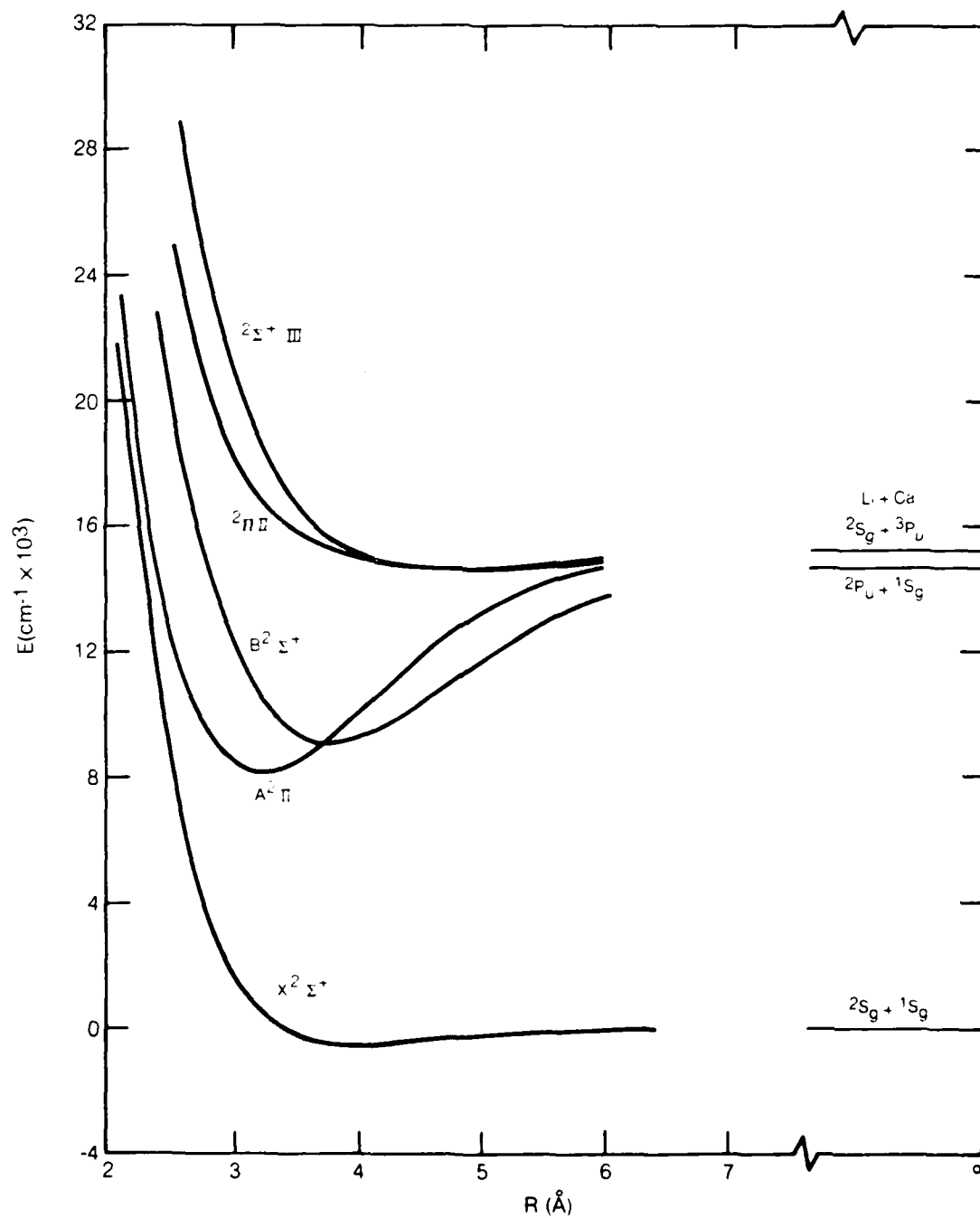
* YANG
(PERTURBATIVE RELATIVISTIC TREATMENT)

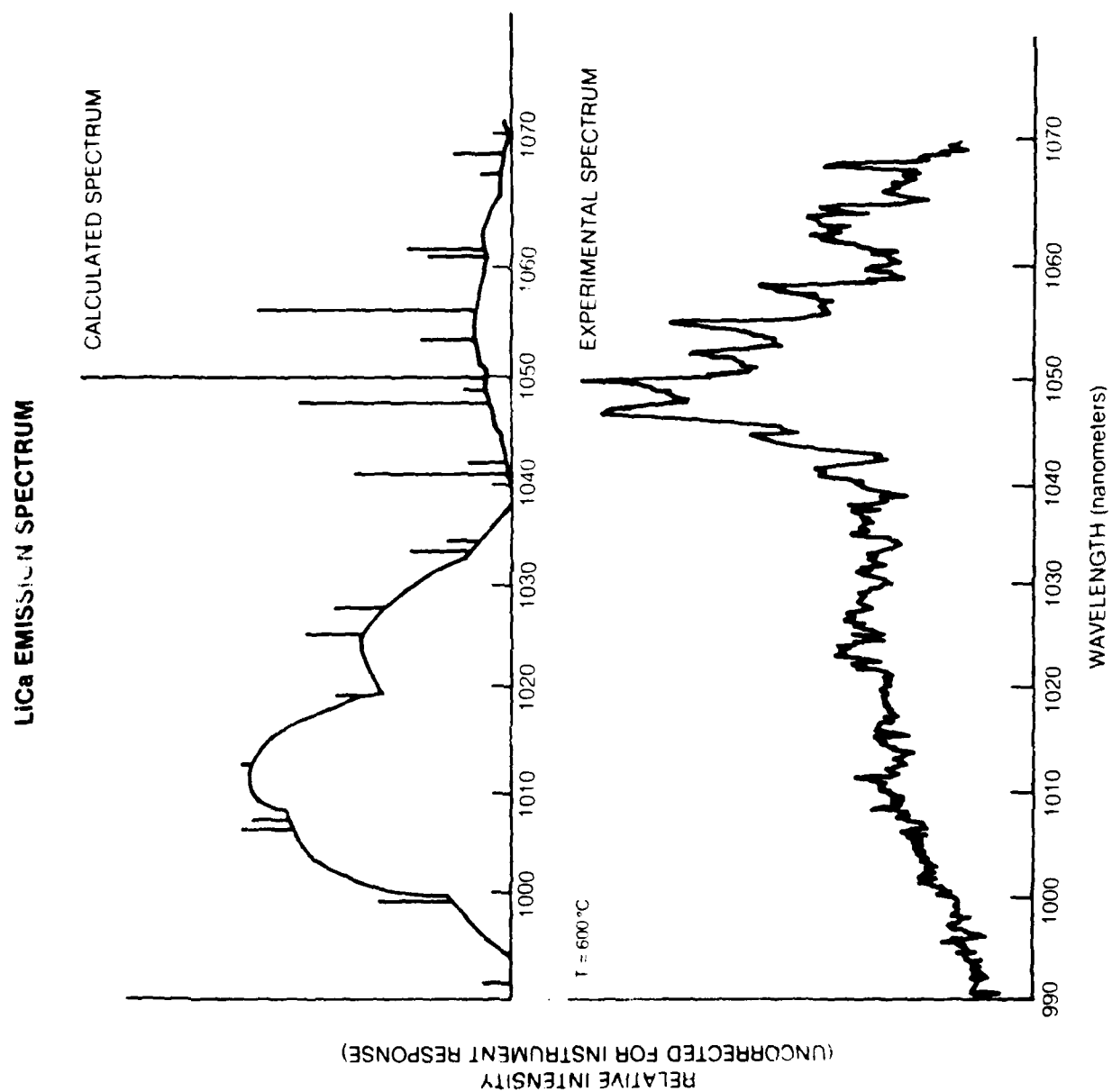
THE $1\Sigma_g^+$ GROUND STATE OF I_2

DENSITY-FUNCTIONAL CALCULATION

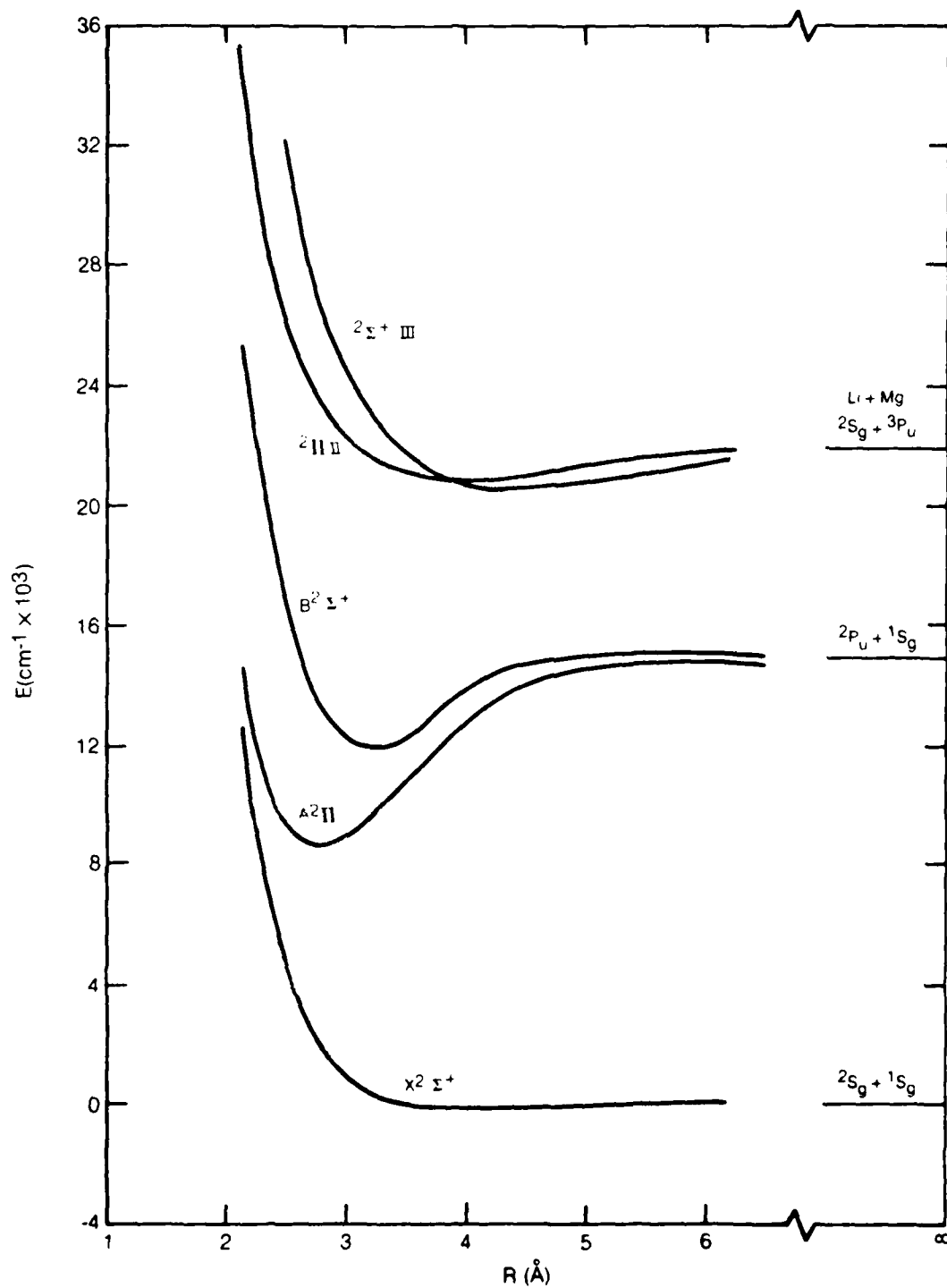


POTENTIAL ENERGY CURVES FOR LiCa

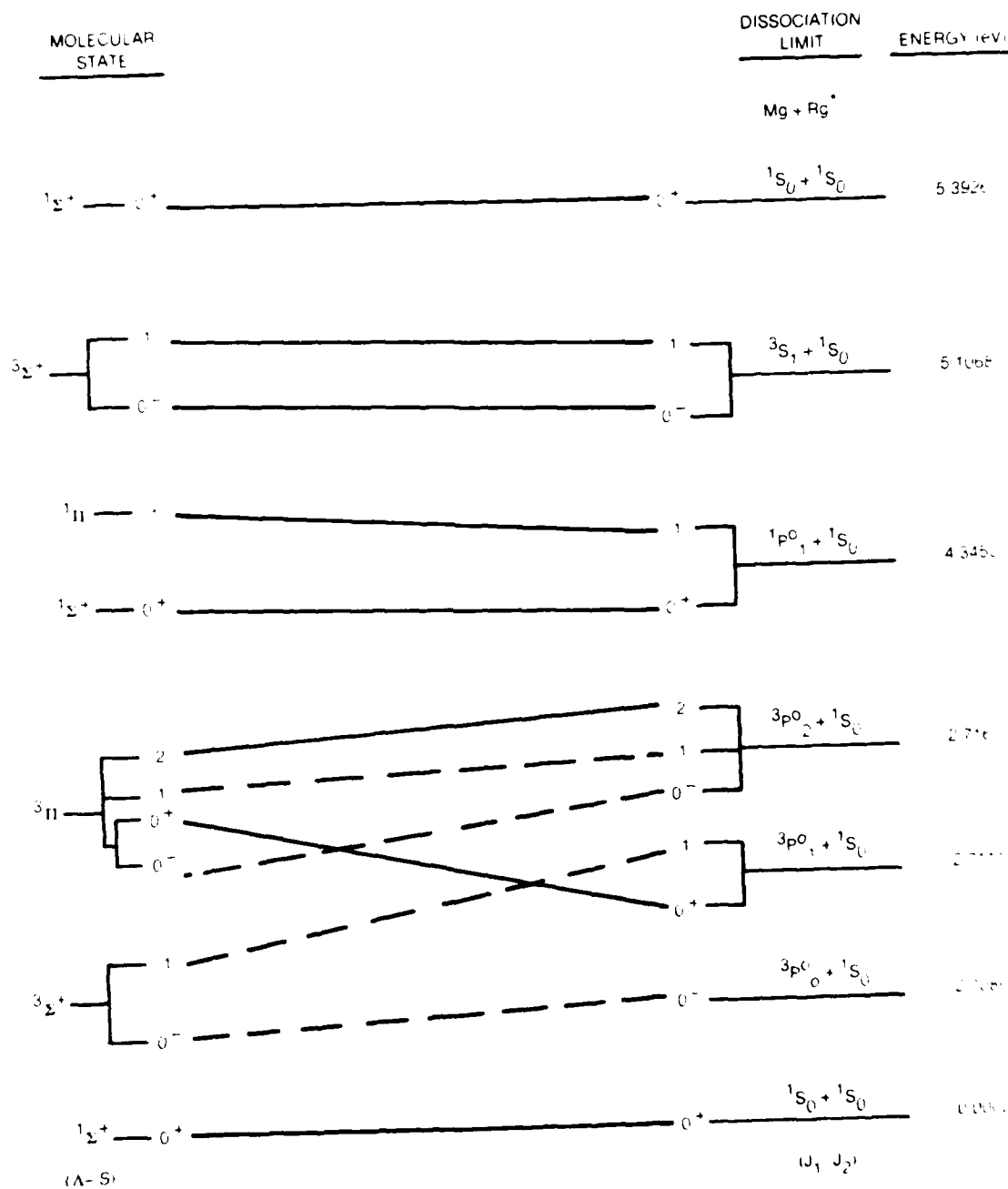




POTENTIAL ENERGY CURVES FOR LiMg

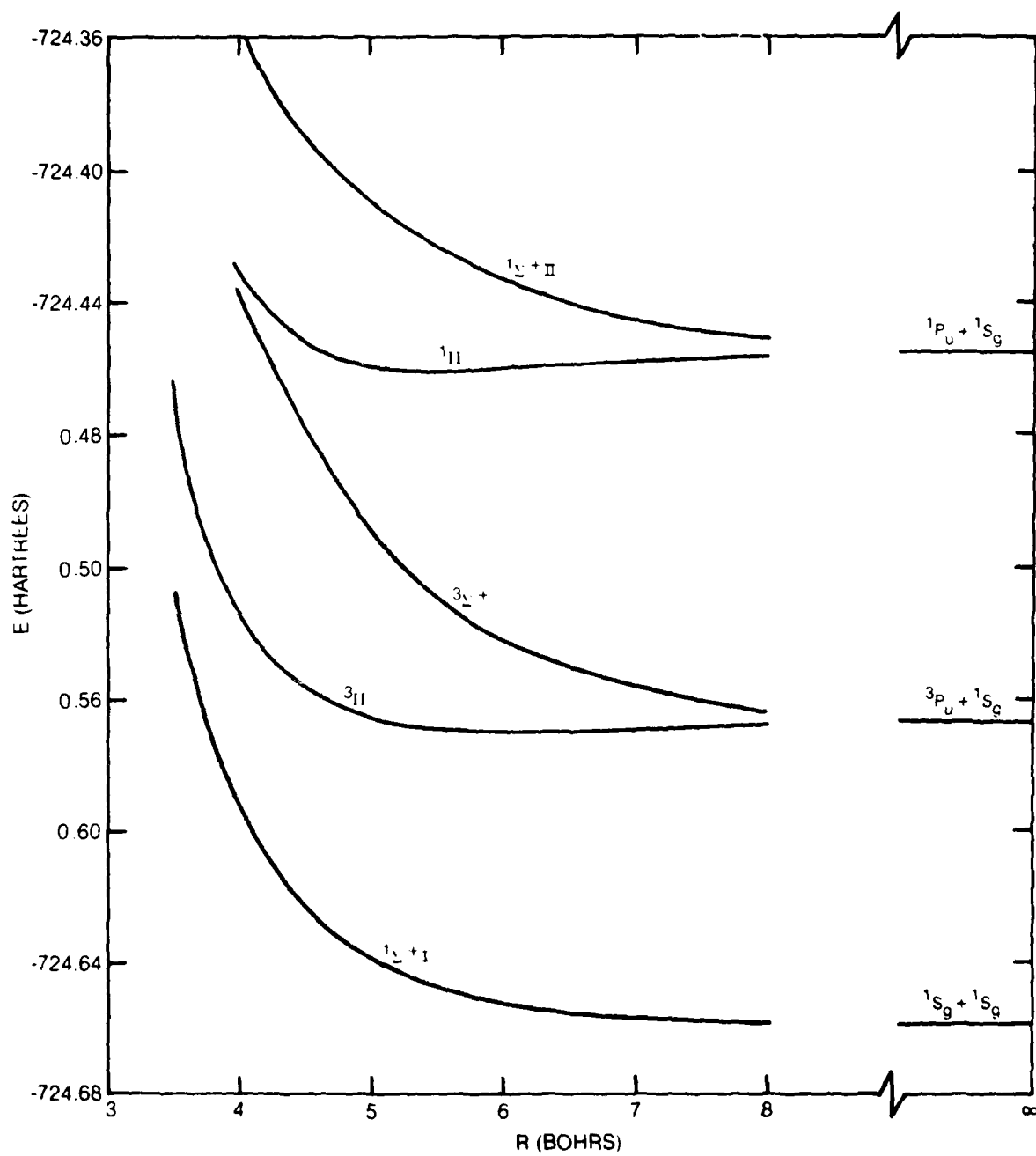


CORRELATION DIAGRAM FOR INTERMEDIATE COUPLING OF THE Mg Rg MOLECULE

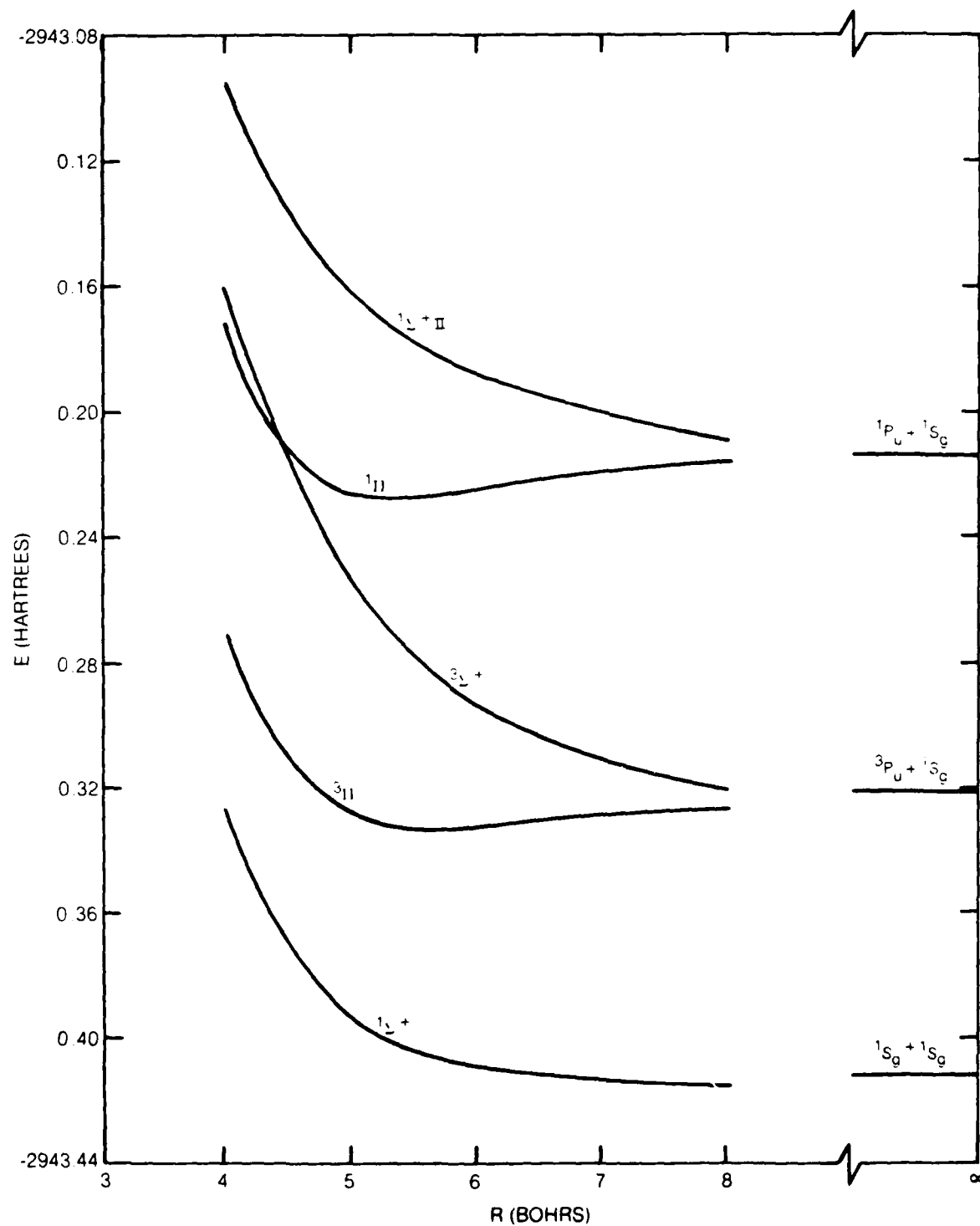


* Rg REPRESENTS A NOBLE GAS ELEMENT (He, Ne, Ar, Kr, Xe)
UNIQUE ASSIGNMENTS FROM (J₁, J₂) TO (Λ-S) COUPLING ARE INDICATED BY SOLID LINES

LOW-LYING POTENTIAL ENERGY CURVES FOR MgAr



LOW-LYING POTENTIAL ENERGY CURVES FOR MgKr



81-3-62-2

TABLE 1
Bond Order Analysis of I_2

MO Configuration	Molecular States	Mo Change	Bond Order
2440*	$X^1\Sigma_g^+$	-	1
2431	$3^1\Pi_u, 1^1\Pi_u$	$a_{\pi} \rightarrow a_{\sigma}$	1^-
2341	$3^1\Pi_g, 1^1\Pi_g$	$b_{\pi} \rightarrow a_{\sigma}$	0
2422	$3^1\Sigma_g^-, 1^1\Delta_g, 1^1\Sigma_g^+$	$(a_{\pi} \rightarrow a_{\sigma})^2$	1^-
1441	$3^1\Sigma_u^+, 1^1\Sigma_u^+$	$b_{\sigma} \rightarrow a_{\sigma}$	0
2332	$3^1\Delta_u, 3^1\Sigma_u^-, 1^1\Sigma_u^+$	$\begin{pmatrix} b_{\pi} \rightarrow a_{\sigma} \\ a_{\pi} \rightarrow a_{\sigma} \end{pmatrix}$	0^-
2242	$1^1\Sigma_u^-, 1^1\Delta_u, 1^1\Sigma_u^+$	$(b_{\pi} \rightarrow a_{\sigma})^2$	-1
1432	$3^1\Sigma_g^-, 1^1\Delta_g, 1^1\Sigma_g^+$	$\begin{pmatrix} a_{\pi} \rightarrow a_{\sigma} \\ b_{\sigma} \rightarrow a_{\sigma} \end{pmatrix}$	0^-
1342	$3^1\Pi_u, 1^1\Pi_u$	$\begin{pmatrix} b_{\pi} \rightarrow a_{\sigma} \\ b_{\sigma} \rightarrow a_{\sigma} \end{pmatrix}$	-1
0442	$1^1\Sigma_g^+$	$(b_{\sigma} \rightarrow a_{\sigma})^2$	-1

*(2, 2, 2, 1, 4, 1, 4, 3, 0, 0)

TABLE 2

Spin-Orbit Coupling In I_2

$$H(R) = H^{\text{vso}}(R) + H^{\text{SO}}$$

vSO Calculated from One-Center Terms Only and Assumed $\neq f(R)$

$\Omega=2u$	$3\Pi_u$	$3\Delta_u$	$1\Delta_u$	$3\Pi'_u$
$3\Pi_u$	$-\alpha$	α	α	0
$3\Delta_u$	α	0	0	$-\alpha$
$1\Delta_u$	α	0	0	α
$3\Pi'_u$	0	$-\alpha$	α	$-\alpha$

$\Omega=0^+_g$	1^+_g	$3\Pi_g$	3^-_g	1^+_g
1^+_g	0	2α	0	0
$3\Pi_g$	2α	α	$\sqrt{2}\alpha$	$-\sqrt{2}\alpha$
3^-_g	0	$\sqrt{2}\alpha$	0	2α
1^+_g	0	$-\sqrt{2}\alpha$	2α	0

$$\alpha = \frac{1}{2} \zeta 5p = 2534.38 \text{ cm}^{-1}$$

TABLE 3

Spectroscopic Constants
For Low-Lying States of I_2

	$X^1\Sigma_0^+$ (experimental)	$A^1\Sigma_{2u}$ (calculated)	$A^3\Pi_{1u}$ (experimental)	$B^3\Pi_0^+$ (experimental)
$\omega_e(\text{cm}^{-1})$	214.502	116.527	94.954	125.697
$\omega_e X_e(\text{cm}^{-1})$	0.6147	0.3368	2.429	0.7642
$R_e(\text{\AA})$	2.6663	3.0056	$(3.12)^{+}_{-}15$	3.0247
$B_e(\text{cm}^{-1})$	0.03737	0.02941	-	0.02904
$\alpha_e(\text{cm}^{-1})$	0.000114	0.00012	-	0.000158
$D_e(\text{cm}^{-1})$	12547.	5870. (A, S) 5790. (J, J)	1640.	4381.
$D_0(\text{cm}^{-1})$	12440.	5812. (A, S) 5732. (J, J)	1595.	4318.
$T_e(\text{cm}^{-1})$	0.0	6677. (A, S) 6757 (J, J)	10907.	15769.

TABLE 4

Reaction for I Atom Production

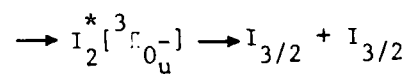
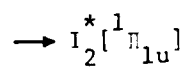
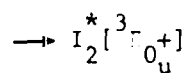
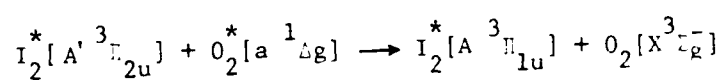
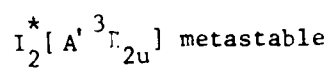
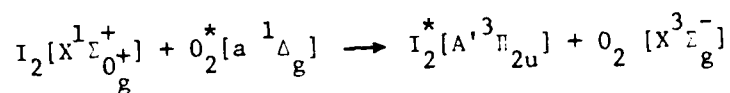


TABLE 5
Correlation Diagram for Group
IA/IIA Bimetals

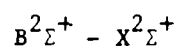
<u>Separated atoms</u> <u>IA + IIA</u>	<u>E (eV)</u>			<u>Molecular states</u>
	<u>LiMg</u>	<u>LiCa</u>	<u>NaMg</u>	
$2s_g + 1s_g$	0.00	0.00	0.00	$2\Sigma^+(1)$
$2p_u + 1s_g$	1.85	1.85	2.10	$2\Sigma^+(1), 2\Pi(1)$
$2s_g + 3p_u$	2.71	1.89	2.71	$2\Sigma^+(1), 4\Sigma^+(1),$ $2\Pi(1), 4\Pi(1)$

TABLE 6
Calculated Spectroscopic Constants for LiCa

State	$T_e(\text{eV})$	$\omega_e(\text{cm}^{-1})$	$\omega_e x_e(\text{cm}^{-1})$	$\alpha_e(\text{cm}^{-1})$	$r_e^0(\text{\AA})$	$B_e(\text{cm}^{-1})$	$D_e(\text{eV})$	$D_0(\text{eV})$
$B^2\Sigma^+$	1.17	197.44	0.96	.0009	.195	3.822	.765	.752
$A^2\Pi$	1.08	252.44	1.29	.0019	.274	3.226	.882	.866
$X^2\Sigma^+$	0.00	93.36	7.32	.0119	.189	3.883	.072	.067

TABLE 7

Calculated Photoemission Spectra for LiCa

 $\lambda(\text{nm}); \text{Int. (energy/sec)}$

v'' \ v'		0	1	2	3
0	λ	1047	1026	1006	987
	Int	1.000	0.154	0.172	0.071
1		1053	1032	1012	992
		0.529	0.075	0.035	0.140
2		1059	1038	1018	998
		0.183	0.452	0.050	0.078
3		1065	1044	1024	1004
		0.029	0.589	0.013	0.002

TABLE 8

LOW-LYING MOLECULAR STATES OF MgNa
AND THEIR DISSOCIATION LIMITS

<u>Dissociation Limits</u>	<u>eV</u>	<u>Molecular States</u>
Mg + Na		
$1S_g(3s^2) + 2S_g(3s)$	0.0	$2\Sigma^+(1)$
$1S_g(3s^2) + 2P_u(3p)$	2.103	$2\Sigma^+(1), 2\Pi(1)$
$3P_u(3s3p) + 2S_g(3s)$	2.712	$2\Sigma^+(1), 4\Sigma^+(1), 2\Pi(1), 4\Pi(1)$
$1S_g(3s^2) + 2S_g(4s)$	3.191	$2\Sigma^+(1)$
Mg ⁺ + Na ⁻		
$2S_g(3s) + 1S_g(3s^2)$	6.975	$2\Sigma^+(1)$

TABLE 9

MOLECULAR CORRELATION DIAGRAM FOR LiMg

<u>Separated Atoms</u>	<u>E(eV)</u>	<u>Molecular States</u>
<u>Li</u> + <u>Mg</u>		
$2S_g(2s) + 1S_g(3s^2)$	0.00	$2\Sigma^+(1)$
$2P_u(2p) + 1S_g(3s^2)$	1.85	$2\Sigma^+(1), 2\Pi(1)$
$2S_g(2s) + 3P_u(3s3p)$	2.71	$2\Sigma^+(1), 4\Sigma^+(1), 2\Pi(1), 4\Pi(1)$
$2S_g(3s) + 1S_g(3s^2)$	3.37	$2\Sigma^+(1)$
$2P_u(3p) + 1S_g(3s^2)$	3.83	$2\Sigma^+(1), 2\Pi(1)$
$2D_g(3d) + 1S_g(3s^2)$	3.88	$2\Sigma^+(1), 2\Pi(1), 2\Delta(1)$
$2P_u(2p) + 3P_u(3s3p)$	4.56	$2\Sigma^+(2), 4\Sigma^+(2), 2\Sigma^-(1), 4\Sigma^-(1),$ $2\Pi(2), 4\Pi(2), 2\Delta(1), 4\Delta(1)$

TABLE 10

Spin-Orbit Coupling in Ca[Mg]-Rg Molecules

$$H(R) = H^{A-S}(R) + V^{S-0}$$

 V^{S-0}

(Assumed Constant Using Atomic Coupling)

	$3P_2$	$3P_1$	$3P_0$	$1P_1$	Atomic Spin-Orbit Matrix
$3P_2$	$\alpha/2$	0	0	0	
$3P_1$	0	$-\alpha/2$	0	$\alpha'/\sqrt{2}$	
$3P_0$	0	0	$-\alpha$	0	
$3P_1$	0	$\alpha'/\sqrt{2}$	0	$E_S - E_T$	

$\Lambda=0^+$		3_{π}	1_{π}^+		$\Lambda=0^-$		3_{π}	3_{π}^+
	3_{π}	$\alpha/2$	$\alpha'/\sqrt{2}$			3_{π}	$-\alpha/2$	$\alpha/\sqrt{2}$
	1_{π}^+	$\alpha'/\sqrt{2}$	0			3_{π}^+	$\alpha/\sqrt{2}$	0

$\Lambda=1$		3_{π}	3_{π}^+	1_{π}		$\Lambda=2$		3_{π}
	3_{π}	0	$\alpha/2$	$\alpha'/2$			3_{π}	$\alpha/2$
	3_{π}^+	$\alpha/2$	0	$-\alpha/2$				
	1_{π}	$\alpha'/2$	$-\alpha/2$	0				

APPENDIX A

ELECTRONIC STRUCTURE OF THE NOBLE GAS DIMER IONS.
III. ABSORPTION SPECTRUM FOR THE $A \ ^2\Sigma_u^+ \rightarrow B \ ^2\Pi_g$ SYSTEM*

H. H. Michels and R. H. Hobbs
United Technologies Research Center
East Hartford, Connecticut 06108

ABSTRACT

A systematic study of the electronic structure and chemical binding of the dimer ion sequence, Ne_2^+ , Ar_2^+ , Kr_2^+ and Xe_2^+ , has been carried out using both density functional and ab initio configuration interaction computational approaches. From the results of this study, the absorption spectrum for the visible/IR transition of the $A \ ^2\Sigma_u^+ \rightarrow B \ ^2\Pi_g$ system has been calculated.

* Supported in part by the Air Force Office of Scientific Research under Contract F49620-80-C-0095.

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APPENDIX B

LASER CHEMILUMINESCENCE OF LiCa^{*}

D. K. Neumann and D. J. Benard
Kirtland Air Force Base
New Mexico 87117

H. H. Michels[‡]
United Technologies Research Center
East Hartford, Connecticut 06108

ABSTRACT

Emission from diatomic LiCa molecules was obtained upon pumping a mixture of Li and Ca vapors with an Ar⁺ ion laser. The excited LiCa molecules were formed via reactions of excited Li₂ dimers with Ca atoms. The LiCa emission was analyzed spectroscopically and found to be in good agreement with a synthetic spectrum derived from ab initio calculations of the LiCa potential energy curves

* Published in Chemical Physics Letters, Vol. 73, 343-347, 1980.

‡ Supported in part by the Air Force Office of Scientific Research under Contract F49620-80-C-0095.

APPENDIX C

POTENTIAL ENERGY SURFACE AND CROSS-SECTIONS FOR THE $H^-(D^-) + H_2(D_2,HD)$
ION-MOLECULE REACTIONS*†

H. H. Michels

United Technologies Research Center, East Hartford, Connecticut 06108

J. F. Paulson

Air Force Geophysics Laboratory, Hanscom Field, Massachusetts 01731

ABSTRACT

A uniform ab initio potential energy surface for the $H^- + H_2$ reaction has been constructed using an optimized double-zeta, plus polarization and diffuse orbital, STO basis set within a configuration-interaction valence bond framework. Calculations in both triangular and linear geometries have been carried out to define the lowest singlet potential energy surface. From our energy contour diagrams we find the minimum energy reaction path for a linear conformation of $H^- + H_2$, in agreement with previous studies of this system. Our calculated barrier height is 15 kcal/mole, a value close to that obtained for the $H + H_2$ reaction using a similar quality basis set. The energy contours for $H^- + H_2$ for the isosceles triangle arrangement of the nuclei indicate that the least energy path leads to dissociation into $H^- + H + H$. Experimental cross sections have been measured for the $H^- + D_2(HD)$ and $D^- + H_2(HD)$ ion exchange reactions in the energy range from 0.5 to 10.0 eV. These data exhibit a threshold of approximately 1 eV and a maximum in the exchange cross section between 2 and 3 eV collision energy.

* This work supported in part by the Air Force Office of Scientific Research

† Published as Chapter 22 in Potential Energy Surfaces and Dynamic Calculations, D. G. Truhlar, ed., Plenum Press, New York, 1981.

**DATA
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